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Glycine: A potential coupling agent to bond to helium plasma treated PEEK?

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Abstract: OBJECTIVES To test the tensile bond strength (TBS) between two self-adhesive resin composite cements and PEEK after helium plasma treatment and used glycine as a potential coupling agent incorporated in different adhesives. METHODS In summary, 896 air-abraded PEEK specimens were fabricated. Half of the specimens were treated with cold active inert helium plasma and the other half were left non-treated. Both groups were then split in two groups: In group 1 (n=256), 64 specimens were pre-treated with: (a) soft-liner liquid, (b) visio.link, (c) Ambarino P60 and (d) no pre-treatment (control), respectively. In group 2 (n=192), specimens were conditioned accordingly, but the adhesive materials were modified by including a commercially available glycine (Air-Flow PERIO). PEEK specimens were then luted using either RelyX Unicem or Clearfil SA Cement and TBS was measured initially and after 14 days water storage combined with 10'000 thermal cycles (16 specimens/subgroup). Fracture type analysis was performed. For statistical analyses Kolmogorov-Smirnov, Shapiro-Wilk tests, 1-, 4-way ANOVA (post hoc: Scheffé), and t-test were used ($p<0.001$). RESULTS Helium plasma pre-treatment without glycine showed no impact on initial TBS ($p>0.348$). In contrast, a combination between glycine application and Softline/Ambarino P60 allowed for significantly higher initial TBS was measured after helium plasma treatment ($p=0.001$). However, this effect was no evident after thermo-cycling. All groups conditioned with visio.link showed the highest TBS values. SIGNIFICANCE The introduction of amine groups by simple provision of amino acids in the form of glycine can improve the bond strength after helium plasma treatment using different adhesive materials. However, using this simple approach, the method cannot withstand thermal challenge yet.

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Glycine: A potential coupling agent to bond to plasma treated PEEK?

Short title: Bond strength to PEEK

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Abstract

Objectives: To test the tensile bond strength (TBS) between two self-adhesive resin composite cements and PEEK after helium plasma treatment and used glycine as a potential coupling agent incorporated in different adhesives.

Methods: In summary, 896 air-abraded PEEK specimens were fabricated. Half of the specimens were treated with cold active inert helium plasma and the other half were left non-treated. Both groups were then split in two groups: In group 1 (n=256), 64 specimens were pre-treated with: a. Soft-Liner Liquid, b. visio.link, c. Ambarino P60 and d. no pre-treatment (control), respectively. In group 2 (n=192), specimens were conditioned accordingly, but the adhesive materials were modified by including a commercially available glycine (Air-Flow PERIO). PEEK specimens were then luted using either RelyX Unicem or Clearfil SA Cement and TBS was measured initially and after 14 days water storage combined with 10'000 thermal cycles (16 specimens/subgroup). Fracture type analysis was performed. For statistical analyses Kolmogorov-Smirnov, Shapiro-Wilk tests, 1-, 4-way ANOVA (post-hoc: Scheffé), and t-test were used ($p<0.001$).

Results: Helium plasma pre-treatment without glycine showed no impact on initial TBS ($p>0.348$). In contrast, a combination between glycine application and Softline/Ambarino P60 allowed for significantly higher initial TBS was measured after helium plasma treatment ($p=0.001$). However, this effect was no evident after thermo-cycling. All groups conditioned with visio.link showed the highest TBS values.

Significance: The introduction of amine groups by simple provision of amino acids in the form of glycine can improve the bond strength after helium plasma treatment using different adhesive materials. However, using this simple approach, the method cannot withstand thermal challenge yet.

1. Introduction

Polyetheretherketone (PEEK), a polymer from the group of polyaryletherketone (PAEK), which comes more and more in the focus of prosthetic dentistry as implant, provisional abutment, implant supported bar or clamp material (RDPs) [1]. It is biocompatible and exhibits good mechanical properties [2]. It displays a rather low surface energy and high resistance to surface modification by different chemical treatments [3, 4] and is therefore stable to nearly all organic and inorganic chemicals. However, it still remains a problem to achieve adequate bond strengths to composite resin materials.

A first study on this topic assessed the bonding potential of a self-adhesive resin composite cement (RelyX Unicem) and an adhesive/composite system (Heliobond/Tetric) to differently pre-treated PEEK surfaces and showed that bonding to PEEK was only possible when using a bonding system on an etched surface using sulfuric acid [5]. However, materials were applied on surfaces etched with sulfuric acid, which - from a clinical perspective – may be hazardous in a clinical setting. Additional methods without etching are therefore still warranted by means of simple and safe surface (pre-)treatment modalities. Among the latter, plasma surface treatment was thought to have a potential to raise the surface energy in order to improve the overall bonding characteristics. The physics definition of “plasma” is an ionized gas with an essentially equal density of positive and negative charges. It can exist over an extremely wide range of temperature and pressure [6]. A previous in vitro study showed that the use of methyl methacrylate (MMA)-based adhesives allowed for bonding between PEEK and self-adhesive resin cements, but helium plasma treatment had no impact on bond to resin composite cements [7]. This was explained – in part – by a lack of sufficient functional groups being able to react with methacrylate, because PEEK represents an organic thermoplastic polymer material with highly cross-linked structures. Therefore, no chemical bonding between substrates could be achieved.

Grace and Gerenser were able to demonstrate the induction of amine and imine carbon species as functional groups on the surface of nitrogen plasma-treated polystyrene [3]. The majority of these functional groups usually contained a terminal nitrogen (primary amine or imine). A previous study hypothesized that the thereby induced functional groups on the surfaces of fibre-reinforced composite posts might contain terminal nitrogen, which then reacted with the functional groups in the composite core build-up material [4] and moreover, that these amine and imine functional groups might remain stable over time as compared to the oxygen functional groups. Indeed, nitrogen plasma treatment appeared to increase the tensile-shear bond strength between post and composite and nitrogen functional groups were apparently induced on the surface, which became more stable.

Based on these findings, we aimed to assess the influence of the application of amine groups by simple addition of amino acids (glycine) on the bond strength after helium plasma treatment and different adhesive material applications to two resin cements. The hypothesis was that the induction of functional groups after helium plasma pre-treatment improves the bond strength properties to resin composite cements - even after a thermal challenge.

2. Material and methods

Eight-hundred-and-ninety-six PEEK specimens (Dentokeep, nt-trading, Karlsruhe, Germany) were cut under water-cooling to a thickness of 2 mm (Secutom50, Struers, Ballerup, Danemark), were embedded in chemically curing acrylic resin (ScandiQuick, ScanDia, Hagen, Germany) and then polished up to silicium carbide paper (SIC) P2400 (PlanoPol-2, Struers) under constant water-cooling. All PEEK specimens were air-abraded with alumina powder with mean size of 50 µm (basic Quattro IS, Renfert, Hilzingen, Germany) at 0.2 MPa for 10 s at 45° angle and were ultrasonically cleaned in distilled water for 5 min. Half of the PEEK specimens (n=448) were treated additionally using low-density cold helium plasma for 20 s with pressure of 0.2 MPa at distance of 10 mm. The other half remained untreated. Afterwards, 64 specimens of each group were adhesively treated with either Soft-Liner Liquid (GC Europe, Leuven, Belgium; group a), visio.link (bredent, Senden, Germany; group b), Ambarino P60 (Creamed, Marburg, Germany; group c) or acted as untreated control group (group d). The treatment was also performed using the same adhesive solutions, which included additionally glycine. For this purpose, 5 g of a commercially available glycine powder (Air-Flow PERIO, EMS, Nyon, Switzerland, Lot.No: 1207053) with 10 ml of the respective adhesive solutions was mixed until homogeneous solution. Table 1 provides and overview regarding the manufacturers, compositions and the single application steps of each adhesive material used in this study according to the manufacturer’s instructions. The allocation of the different experimental groups and subgroups is depicted in Figure 1.

Subsequently, acrylic cylinders (inner diameter of 2.9 mm) were filled with either a self-adhesive resin composite cement RelyX Unicem (3M ESPE, Seefeld, Germany) or Clearfil SA Cement (Kuraray Medical Inc. Sakazu, Kurashiki, Okayama, Japan) for each subgroup (N=32). The filled cylinders were positioned on the PEEK surface and luted applying a standardized load of 100 g on the PEEK surface. Excess resin composite cement was carefully removed from the bonding margin using microbrushes (3M ESPE).

Specimens were then stored in distilled water at 37°C in an incubator (HeraCell 150, Heraeus, Hanau, Germany). Half of the specimens was removed after 24 h (n=16) and the tensile bond strength was tested, whereas the other half (n=16) was additionally aged for another 14 days and additionally thermo-cycled for 10,000 cycles between 5°C and 55°C with a dwell time of 20 s each distilled water bath (Thermocycler THE 1100, SD Mechatronik, Feldkirchen-Westerham, Germany).

For the tensile bond strength measurements, specimens were tested in a Universal Testing Machine (Zwick 1445, Zwick, Ulm, Germany) and pulled with a crosshead speed of 5 mm/min [8] as depicted in Figure 2. Tensile bond strength (TBS) was calculated as follows: fracture load/ bonding area = N/mm^2= MPa.

For fracture type analysis, the debonded area was examined directly after TBS tests under an optical microscope at a magnification of 25x (Wild M3B, Heerbrugg, Switzerland). Failure types were determined as follows: a) adhesive (no cement remnants left on the PEEK surface), b) mixed (cement remnants partially left on PEEK with PEEK surface exposed) and c) cohesive failures.

For the data analysis descriptive statistics were calculated. Normality of data distribution was tested using Kolmogorov-Smirnov test. Analysis of variance was performed with respect to helium plasma treatment, glycine agent, adhesive system, resin composite cement and aging level. Unpaired t-test was used for calculation of impact of aging type. P values smaller than 5% were considered to be statistically significant in all tests. The data were analyzed using SPSS Version 20 (SPSS INC, Chicago, IL, USA).

3. Results

Kolmogorov-Smirnov test indicated no violation of the assumption of normality. Interaction (helium plasma treatment vs. glycine agent vs. adhesive system vs. resin cement vs. aging level) showed an overall significant impact on the results ($p<0.001$). Therefore, the fixed effects helium plasma treatment, glycine agent, adhesive system, resin cement and aging level cannot be compared directly as the higher order interactions were found to be significant. Consequently, several different analyses were provided and splitted at levels of helium plasma treatment, glycine agent, adhesive system, resin cement and aging level. The results of this study expressed as mean tensile bond strength (MPa) with standard deviations of all tested groups are presented in Table 2. Hereafter, the results are described separately according to the different impacts:

Impact of helium plasma treatment

Within groups without glycine application no impact of helium plasma pre-treatment on initial TBS was observed ($p>0.348$), regardless on the resin composite cement used. In contrast, within combination between glycine application and Softline/Ambarino P60 significantly higher initial TBS was measured after helium plasma treatment ($p=0.001$). Groups conditioned with glycine and visio.link showed significantly lower initial TBT after helium plasma pre-treatment ($p>0.001$).

In exception of glycine conditioned and cemented using Clearfil SA Cement group, no helium plasma treated in combination with visio.link groups showed significantly higher aged TBS than the groups with helium plasma treatment. The remaining adhesive systems showed no bond (0 MPa).

Impact of glycine agent

In general, visio.link in combination with glycine agent presented a significantly decrease of TBS values ($p<0.015$). In contrast, glycine combined with Soft Liner or Ambarino P60 increased the initial TBS on PEEK specimens after helium plasma treatment. Another groups showed no impact of glycine agent.

Impact of the adhesive system

Visio.link showed the highest TBS in all tested groups ($p<0.001$). In contrast, visio.link, Ambarino P60 and groups without conditioning showed no bond (0 MPa). Only when helium plasma treatment was performed, and glycine was included, Ambarino P60, Soft Liner and visio.link showed initial TBS of 3.1, 5.5 and 13.7 MPa, respectively.

Impact of resin cement

No influence of the resin cement was observed ($p>0.05$).

Failure types

Failure type analysis revealed adhesive failures in all groups after TBS testing. No cohesive failures were observed.

4. Discussion

This study assessed to potential of glycine when incorporated into different adhesive materials to enable bonding of self-adhesive resin composite cements to PEEK after helium plasma treatment. The idea to conduct this study was based on our previous findings that in-vitro study showed that helium plasma treatment had no impact on bond to resin composite cements [7], which was explained – in part – by a lack of sufficient functional groups being able to react with methacrylate. Nitrogen plasma treatment has already been shown to induce amine and imine carbon species as functional groups on polystyrene surfaces [3] displaying terminal nitrogen. Another study hypothesized that thereby induced functional groups on the surfaces of fibre-reinforced composite posts might also contain terminal nitrogen, which then reacts with the functional groups in the composite core build-up materials itself [4] and moreover, that these amine and imine functional groups might remain stable over time as compared to functional oxygen groups. Indeed, nitrogen plasma treatment appeared to increase the tensile-shear bond strength between post and composite and nitrogen functional groups were apparently induced on the surface, which became more stable.

Glycine is the smallest of the 20 amino acids and commonly found in proteins. It is a colorless, sweet-tasting crystalline solid and is used in dentistry mainly in powder form for the cleaning of teeth and implants [9-11]. In pre-tests, we used commercially available powders to sandblast and thereby conditioning PEEK surfaces, given the hypothesis that this surface pre-treatment, like a silication, could allow for adequate bonding between PEEK and a given adhesive material. Since glycine powders display a minimal abrasiveness and therefore not lead to distinctive surface changes in terms of roughening, the additional additive chemical modification as intended failed to result in any effective bonding (unpublished data). Therefore, we tried to incorporate glycine into adhesive materials by simply mixing commercially available powders into adhesive materials. And indeed, pre-tests with PMMA-based adhesives showed remarkable bond strength as compared to the adhesives without incorporated glycine. It must be noted that the materials used for this first feasibility and stability study were far away from any market-ready product. As a shortcoming, the simple mixing procedure has to be mentioned. In addition, there is no information the required concentration and which ratio is optimal for such a claimed approach. The evaluation of different concentration, however, would have been far beyond the scope of this study, which already used more than 800 specimens. But we could demonstrate the incorporation of glycine in Soft Liner and Ambarino P60 in combination with a helium plasma pre-treatment was able to establish initial bond strengths ranging from 2.3 to 13.7 MPa on using both cements. However this effect was not long-lasting, because after storage and thermo-cycling no bond strength was measurable. We suspect that the leakage at the interface may have hampered a stable bonding. In addition, the materials may have encountered some air entrapment and the achieved homogeneity of the self-made materials was most probably not ideal as well. The latter may also explain the fact, that glycine-modification reduced the bond strengths on visio.link. Nevertheless, as a proof-of-principle, our data suggest that the glycine approach may lead to a potential solution with regard to persisting problems of bonding to PEEK even with helium plasma pre-treatment. Still, technical improvements and modifications are needed.

The highest initial and aged TBS values were observed within groups' conditioned using visio.link. It seems that MMA monomers are important contributors of increased bond strength between PEEK and another dimethacrylate-based materials. This was also supported by numerous previous studies [7, 8, 12]. Visio.link contains MMA monomers, PENTIA and dimethacrylate. Therefore, it can be assumed that MMA caused the PEEK surface to swell and that the dimethacrylate monomers provided the connection to the resin composite cements with two carboxyl groups as binding sites. However, MMA is not enough for adequate bonding properties. Soft Liner (MMA solution) showed without an additional pretreatments no bond strengths values. Therefore, it is likely that the few shares of PETIA and the dimethacrylate contained in visio.link, lead to the improvement of the TBS. Also a dimethacrylate based on phosphor acid esters and phosphon acid esters solution as Ambarino P60 can without MMA monomers can not produce a bond between PEEK and resin composite.

The study results, however, display a promising approach to improve the bonding capacity - at least after initial evaluation - of PEEK in combination with helium plasma treatment when using glycine as a coupling promoter. This could be an option to optimize adhesive protocols in the future to facilitate bonding and maybe ensure adequate stability even after thermal and mechanical stressing. This field is now open for scrutiny.

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Tables and Figures

Table 1. Summary of veneering resins and adhesive materials evaluated.

Table 2. Results of three-way ANOVA interaction between veneering resin vs. adhesive vs. aging level.

Table 3. Mean, SD and 95% confidence interval of TBS of three different veneering resins on air-abraded and subsequently pretreated PEEK surfaces [MPa].

Figure 1: Summary of test groups division according helium plasma treatment, conditioning and resin composite cement.

Table 1. Summary of veneering resins and adhesive materials evaluated.

Materials	Product Name	Manufacturer	Composition	Application steps as recommended by the manufacturer	Lot.No	Curing light used*
Adhesive systems	Soft-Liner Liquid	GC Europe, Leuven, Belgium	MMA, BPBG, DBP, EtOH	Apply on PEEK surface and leave for 120 s	1204042	-
	visio.link	Bredent, Senden, Germany	MMA, PETIA, dimethacrylates, Photoinitiators	1. Apply adhesive on the PEEK surface with a brush 2. Light cure for 90 s	114784	Brelux Power Unit, Bredent
	Ambarino P60	Creamed, Marburg, Germany	Dimethacrylate based on phosphor acidesters and phosphon acidesters	Apply on PEEK surface and leave for 120 s	2011004057	-
Self-adhesive resin cement	RelyX Unicem Automix 2	3M ESPE, Seefeld, Germany	methacrylated phosphoric esters, dimethacrylate organic fillers	1. light cure for 40 s	475760	
	Clearfil SA Cement	Kuraray Medical Inc. Sakazu, Kurashiki, Okayama, Japan	Bis-GMA, TEGDMA, MDP, organic fillers	1. light cure for 40 s	033BBA	

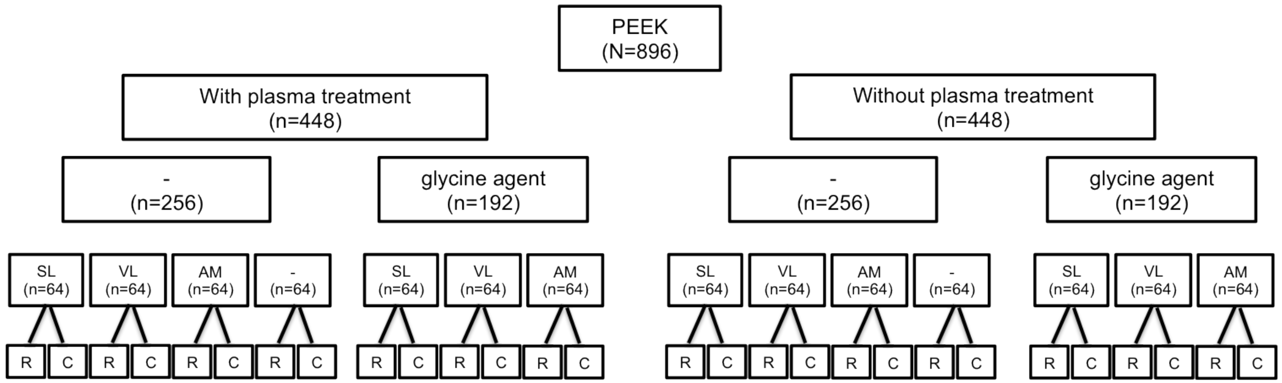
* all polymerization lights were chosen according to manufacturer´s specific instructions

Table 2: Mean tensile bond strength with standard division (MPa) of all tested groups.

Pre-treatment			**Cementation (non-aged)**		**Cementation (aged)**	
Helium **Plasma** application	**Glycine** application	**Adhesive** material	RelyX Unicem Automix	Clearfil SA Cement	RelyX Unicem Automix	Clearfil SA Cement
Yes	No	Soft Liner	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0(0)^{a}
		visio.link	18.6 (4.9)^{b}	19.9 (3.0)^{b}	14.4 (4.5)^{b}	17.5 (6.2)^{b}
		Ambarino P60	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0(0)^{a}
		None	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0 (0)^{a}
	Yes	Soft Liner	5.5 (1.7)^{b}	4.7 (1.4)^{b}	0 (0)^{a}	0 (0)^{a}
		visio.link	13.7 (3.5)^{c}	12.6 (2.8)^{c}	3.6 (5.6)^{b}	9.8 (4.0)^{b}
		Ambarino P60	3.1 (1.0)^{b}	2.3 (1.1)^{b}	0 (0)^{a}	0 (0)^{a}
		None	0 (0)^{a}	0 (0)^{a}	0 (0)^{a}	0 (0)^{a}
No	No	Soft Liner	0 (0)^{a}	0 (0)^{a}	0 (0)^{a}	0(0)^{a}
		visio.link	19.4 (3.8)^{b}	21.1 (4.2)^{b}	19.0 (6.1)^{b}	19.3 (6.9)^{b}
		Ambarino P60	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0(0)^{a}
		None	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0 (0)^{a}
	Yes	Soft Liner	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0(0)^{a}
		visio.link	17.4 (4.0)^{b}	16.4 (2.5)^{b}	14.9 (5.6)^{b}	12.8 (3.7)^{b}
		Ambarino P60	0 (0)^{a}	0(0)^{a}	0 (0)^{a}	0(0)^{a}
		None	0 (0)^{a}	0 (0)^{a}	0 (0)^{a}	0 (0)^{a}

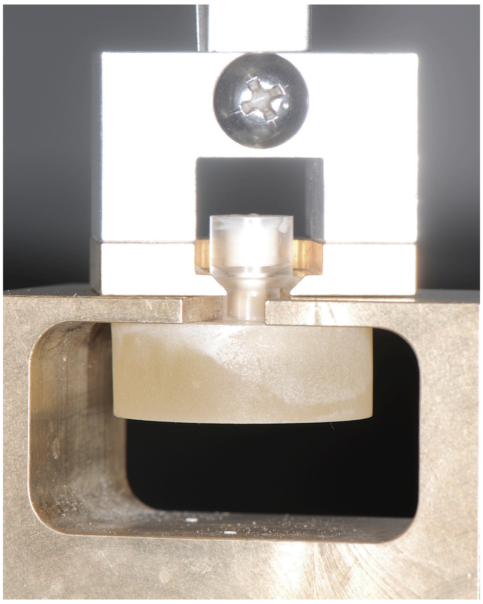
^{abc}different letters presented significantly differences between the adhesive materials within a resin cement, aging level, glycine and helium plasma application.

Figure 1: Summary of test groups division according helium plasma treatment, conditioning and resin composite cement.



- SL: Soft Liner, VL: Visio.link, AM: Ambarino P60
- R: RelyX Unicem, C: Clearfil SA Cement

Figure 2: Tensile bond strength test method.



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